Estimates of Non-Ideal Effects on the Friction Coefficient of Agglomerates

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ABSTRACT

There are several characteristics of silver agglomerates that are not incorporated in existing models for agglomerate dynamics. These characteristics include particle alignment in the electric field, necking between particles, polydispersity of the primary particles, and variable primary sphere size. Estimates of these features on the agglomerate dynamics were computed as perturbations to the Chan-Dahneke agglomerate model. The variable primary sphere size effect results in the largest change from the idealized model with about a 10% increase in scaling exponents for both friction coefficient – number of primary particles ($\eta$) and mass-mobility diameter ($D_{fm}$). The second largest change is a 4% decrease in the exponent $\eta$ and a 4% increase in the exponent ($D_{fm}$) from the alignment in the electric field. The effects of necking between particles and polydispersity of the primary particles are negligible for the two exponents. The combined effect, excluding the variable primary particle size, results in a 17.5% decrease in the dynamic shape factor for agglomerates with a 300 nm mobility diameter. Adjusting the model by this amount provides a significant improvement in the agreement between the model and silver agglomerate measurements for the dynamic shape factor. Experimentally the number of primary spheres is determined from the mass of the agglomerate assuming a constant primary sphere diameter. The predicted apparent exponent $\eta$ based on a 10% variability in the primary sphere size is about a 5% less than the apparent exponent assuming a constant primary sphere size. This is a significant effect relative to the observed 15% decrease in $\eta$ (Shin et al., 2009a) as the agglomerate size increases from the free molecular regime into the transition regime.

Keywords: Dynamic shape factor; Friction coefficient; Mass-mobility diameter scaling exponent.

INTRODUCTION

Atmospheric and intentionally produced aerosol particles are often nonspherical. Soot agglomerates are a type of nonspherical particles that are often found in the ambient aerosol (Katrinak et al., 1993). TiO$_2$ and Ag particles in industrial applications also have agglomerate morphologies (Pratsinis, 1998; Ku and Maynard, 2006). The physical and chemical characterization of nonspherical and fractal particles is an important area of current aerosol research (Friedlander and Pui, 2004).

It is of interest to make use of analytical models to predict structural and dynamic properties of nanoparticle agglomerates such as dynamic shape factor $\kappa$, friction coefficient $f$, number of primary particles $N$, and mass-mobility diameter scaling exponent ($D_{fm}$). Chan and Dahneke (1981), Meakin et al. (1989), and Mackowski (2006) have obtained the friction coefficient of agglomerate particle consisting of many primary spheres by doing numerical simulations in the free molecular regime.

In our recent studies (Shin et al., 2009a, b), mass of silver agglomerates was measured in mobility size range of 80 to 300 nm using a differential mobility analyzer (DMA) together with aerosol particle mass analyzer (APM) (Shin et al., 2009a) and volume of silver agglomerates was measured in mobility size range of 30 to 300 nm using tandem differential mobility analyzers (TDMA) (Shin et al., 2009b). In those studies, we experimentally showed that the deviation between the predicted and measured value of dynamic shape factor for silver agglomerates increases with particle size to a value of about 30%. Also, the exponent $\eta$, which characterizes the friction coefficient on the number of primary spheres, decreases as the range of number of primary spheres is increased from less than...
about 50 to 50 to 600 primary spheres. On the other hand, model predictions (Chan and Dahneke, 1981; Meakin et al., 1988) indicate that \( \eta \) is independent of the range in the number of primary spheres.

The numerical simulation referenced above considers nanoparticle chain agglomerates of low fractal dimension as model agglomerates in the free molecular flow regime. The model agglomerates were assumed to be randomly aligned consisting of touching spheres with the same diameter with no necking between the primary particles. However, the agglomerate particle shown in Fig. 1 does not match the assumptions for the numerical simulation referenced above: (1) The agglomerates may not be randomly aligned. Studies have shown that agglomerates can be partially aligned in electric fields (Kousaka et al., 1996; Zelenyuk and Imre, 2007). (2) It is not a loose ("neckless") agglomerate. Neck formation can occur in silver agglomerates (Weber and Friedlander, 1997; Lall et al., 2006). (3) Primary particles are not monodisperse. (4) The primary particle size may vary with the size of the agglomerate. Because of these differences, it is of interest to estimate the effects resulting from the difference between model agglomerates such as considered by Chan and Dahneke (1981), Meakin et al. (1989), and Mackowski (2006) and actual agglomerates such as the recently studied silver agglomerates (Shin et al., 2009a, b). The goal is to provide insight regarding which non-ideal effects are likely to have the largest effect on the dynamic shape factor and on scaling law exponents. In this study, perturbations of the Chan and Dahneke’s model are computed to estimate these non-ideal effects on the predicted values of dynamic shape factor \( \kappa \) and on the two exponents, \( \eta \) and \( D_{fm} \), for the power law dependence of friction coefficient on the number of primary spheres and of the mass on the mobility diameter.

**PREDICTIONS OF NON-IDEAL EFFECTS BASED ON THE CHAN-DAHNEKE MODEL**

We use the simplest of the three models, the Chan-Dahneke model for a straight chain agglomerate as our basic model. Chan and Dahneke (1981) used a Monte Carlo approach to compute the friction coefficient of a straight chain of spherical particles in the free molecular limit based on the Knudsen number of the primary particle diameter \( K_n = 2\lambda/d_p \), where \( \lambda \) = the mean free path of the gas and \( d_p \) = the primary particle diameter. The following expression is obtained for the friction coefficient:

\[
f = \left( c_{bcs} (N - 1) + c_{ph} \right) \mu \lambda d_p^2 / 4 ,
\]

where \( c_{bcs} \) is the dimensionless friction coefficient for a basic chain unit, two hemispheres touching at their poles, \( N \), the number of spheres in the chain, \( \mu \), the gas viscosity, and \( c_{ph} \) the dimensionless friction coefficient for a sphere. Assuming 7% of the collisions to have specular reflections and 93% diffuse reflections, Dahneke (1982) obtained values of 9.17 for \( c_{bcs} \) if the chain is randomly oriented, and 6.62 for \( c_{bcs} \) if the chain is aligned in the direction of the chain motion, and 11.44 for \( c_{ph} \).

The quantities of interest are the dynamic shape factor \( \kappa \), the exponent \( \eta \) characterizing the power law dependence of the friction coefficient on \( N \), and the mass-mobility diameter scaling exponent \( D_{fm} \). This dynamic shape factor is equal to the ratio of the friction coefficient of the agglomerate, \( f \), to the friction coefficient of a sphere with the same condensed phase volume as the agglomerate:

\[
\kappa = \frac{f}{f_{ve}} = \frac{f C(d_m)}{3\pi \mu d_{ve}} ,
\]

where the subscript \( ve \) refers to the volume equivalent sphere and \( C \) the Cunningham slip correction. The volume equivalent sphere is computed from \( N \) and \( d_p \) as:

\[
d_{ve} = N^{2/3} d_p
\]

The following equations define the exponents \( \eta \) and \( D_{fm} \):

\[
f = AN^\eta
\]

\[
m = k_m d_m^{D_{fm}}
\]

where \( A \) is a prefactor, \( m \) mass of agglomerate, \( k_m \), a prefactor, and \( d_m \), mobility diameter. The quantity \( d_m \) is the diameter of a sphere with the same mobility as that of the agglomerate:

\[
Z_{agg} = \frac{e}{f} = \frac{e C(d_m)}{3\pi \mu d_m}
\]

The mass of the agglomerate is computed using the density \( \rho \) and \( N \):

\[
m = \frac{\pi}{6} d_p^3 / \rho N
\]
Alignment Effect

The mobility diameter of a nonspherical particle is a function of the particle shape and orientation. The electric field in the DMA can cause nonspherical particles to partially align. The torques arising from the free charge on the agglomerate as well as from the induced polarization causes the alignment. For larger agglomerates where the orientation energy is large compared to $kT$, the particle alignment leads to a reduction in the friction coefficient. This reduction will in turn result in a reduction of the dynamic shape factor relative to the value for a random orientation, which is assumed for our baseline calculation.

Here we make an order of magnitude estimate of this change for an agglomerate with $d_m$ equal to 300 nm. We assume the agglomerate has a cross structure with the long chain 1.6 times longer than the short chain. Data for silver agglomerates indicates that the ratio of the maximum projected length divided by the maximum projected width is about 1.6 (Kim et al., 2008). We assume a primary sphere size of 16.2 nm. We use the Chan and Dahneke’s expression for the friction coefficient for both the vertical and horizontal chain. The two chains have one sphere in common. It is assumed that half of this sphere is associated with the longer chain and half with the shorter resulting in the following modification to Chan and Dahneke’s expression for each chain:

$$f = \left( c_{\text{ew}} \left( N_k - 1 1/2 \right) + c_{\text{yp}} \right) \mu \frac{d_p^2}{4 \lambda},$$

where $k = 1, 2$ corresponds to the long and short chain.

For a randomly oriented cross with 201 spheres, 126 in the long direction and 76 in the short direction with one sphere shared, we find that the friction coefficient corresponds to a mobility size of 300 nm. For an aligned cross with 220 spheres, 136 in the long direction and 85 in the short direction with one sphere shared, is aligned in the direction of the longest arm of the cross, we find that the friction coefficient corresponds to a mobility size of 300 nm. The value of $k$ is computed from Eqs. (2) and (3) for both the randomly oriented cross and the aligned cross. It is found that the dynamic shape factor is about 5% smaller for the oriented configuration, 5.78, compared to the random configuration, 6.06. Our method of estimating the alignment effect is similar to that used by Rogak et al. (1993).

As the agglomerate size decreases, the tendency to orient decreases. We assume that for a mobility size of 50 nm, which corresponds to 10 spheres, the orientation is random. Fig. 2 shows the effect of alignment on the dynamic shape factor.

We also estimated how this change in orientation would affect the power law expression for the friction coefficient versus $N$ and for the mass-mobility diameter scaling exponent $D_m$. The exponents were computed based on two points: one for $N = 10$ for the cross in a random orientation and the second for $N = 201$, for which both a random orientation and an aligned orientation are computed. The exponent $\eta$ decreases by 4.3% from a value of 1.00 for the aligned orientation versus a random orientation. For the $D_m$, it is found that the exponent $D_m$ increases by 3.9% from 1.675 to 1.740 as shown in Table 1.

Necking of Particles

As indicated in Fig. 1, the primary spheres making up the agglomerates are not distinct spheres touching at one point. There is a neck between the spheres. In some areas the agglomerate appears more like a rope than a chain of spheres. An extreme version of necking would be the formation of a cylinder. It is of interest to compare the dynamic shape factor and exponent $D_m$ for a chain and a cylinder. In this comparison we take the sphere diameter and cylinder unit length to be 16.2 nm, and choose the cylinder diameter to give the same mass per length as the sphere. The friction coefficient for a cylinder with flat ends in the free molecular limit is given by Dahneke (1973):

$$f(\text{cylinder}) = \frac{\pi \mu d^2}{2 \lambda} \left\{ \left( \frac{L_c}{d_{cy}} + \frac{1}{2} \right) f_c + \left( 2 - \frac{6}{4} f_c \right) \right\} \left[ \frac{L_c}{d_{cy}} \sin^2 \theta + \cos^2 \theta \right],$$

where $d_{cy}$ is the diameter of cylinder, $L_c$ the length of cylinder, $f_c$ the fraction of molecules diffusely reflecting from the particle surface, and $\theta$ the angle between the polar axis of cylinder and flow direction. The relation between the primary sphere diameter, $d_m$, and the cylinder diameter, $d_{cy}$, is given by:

$$d_{cy} = (2/3)^{1/2} (d_m).$$

The friction coefficient of a randomly oriented cylinder can be obtained from the friction coefficients computed about the three principle axes for the orientation dependent friction coefficient. These axes correspond to the cylinder.
Table 1. Change in dynamic shape factor and the exponents $D_{fm}$ and $\eta$ for the mobility diameter of the baseline agglomerates in the range of 100 nm to 300 nm

<table>
<thead>
<tr>
<th>Effects</th>
<th>Average $\kappa$ (after)</th>
<th>$D_{fm}$ (before)</th>
<th>$\Delta D^a$</th>
<th>$\eta$</th>
<th>$\Delta \eta^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alignment</td>
<td>0.977$^b$</td>
<td>1.675$^b$</td>
<td>0.065$^b$</td>
<td>1.0</td>
<td>−0.043$^b$</td>
</tr>
<tr>
<td>polydispersity</td>
<td>0.975</td>
<td>1.554</td>
<td>0.003</td>
<td>1.0</td>
<td>0.000</td>
</tr>
<tr>
<td>necking</td>
<td>0.866</td>
<td>1.554</td>
<td>0.006</td>
<td>1.0</td>
<td>−0.0091</td>
</tr>
<tr>
<td>variable primary size</td>
<td>0.948</td>
<td>1.554</td>
<td>0.081</td>
<td>1.0</td>
<td>0.0124</td>
</tr>
</tbody>
</table>

$^a \Delta D = D_{fm\text{(after)}} - D_{fm\text{(before)}}$ and $\Delta \eta = \eta\text{(after)} - \eta\text{(before)}$

$^b$ $D_{fm}$ for the case of alignment where there is a cross structure is different from 1.554 because only two data points for 50 nm and 300 nm sizes are considered.

orientated in the direction of the field and the two axes orthogonal to the aligned direction. The resulting expression for the friction coefficient of a randomly oriented cylinder $f_{\text{random}}$ (cylinder) is given by Dahneke (1973):

$$f_{\text{random}} \text{(cylinder)} = \frac{3}{[1/f(\theta = 0) + 2/f(\theta = \pi / 2)]}$$  \hspace{1cm} (11)

The two orthogonal axes have identical expression for the friction coefficient.

From Eqs. (9) and (11), one can compute $f_{\text{random}}$ as a function of the length of the cylinder. The ratio of the dynamic shape factor for the cylinder to the dynamic shape factor for a chain of spheres with the same mass is shown in Fig. 2. The cylinder and the chain of spheres have the same length and volume as the chain of spheres. The ratio is initially larger than 1.0 and then decreases asymptotically for large $N$ or large mobility diameter to a value of about 0.86. The cylinder and the chain of spheres have nearly identical values of the friction coefficient for the orthogonal orientation; however, the friction coefficient in the aligned direction is about 30% smaller for the cylinder compared to the chain.

It is seen in Eqs. (1) and (9) that the friction coefficient for both the chain of spheres and the cylinder become proportional to the number of spheres for large $N$ so that it is not surprising that $\eta$ is changed by less than 1% for a chain versus a cylinder as indicated in Table 1. The mass-mobility diameter scaling exponent $D_{fm}$ also is only slightly different for the cylinder compared to the chain.

Polymodispersity of Primary Sphere Size

In comparing with experiment, the Chan and Dahneke expression for the friction coefficient, Eq. (1), was expressed in terms of $N_{mp}$, which is the ratio of the mass of the agglomerate to the mass of a primary sphere. The subscript $mp$ refers to monodisperse. This estimation of $N$ is correct if the primary spheres are monodisperse. In reality, the estimated standard deviation of the primary spheres is about 20% of the mean size. Below, we estimate the effect of the polydispersity on $\kappa$ and $D_{fm}$.

For a distribution of primary sphere sizes, we replace $d^2$ in Eq. (1) with the projected area diameter of the two touching spheres, $(d_{p1}^2 + d_{p2}^2)/2$. We assume that the value of $c_{mp}$ and $c_{bcu}$ are unchanged. The expression for $f_{\text{poly}}$ for a polydisperse distribution of primary spheres is computed as:

$$f_{\text{poly}} = \mu \int \cdots \int \left[ c_{mp} d_{p1}^2 + c_{bcu} \left( d_{p1}^2 + d_{p2}^2 \right) + \cdots \right] d d_{p1} \cdots d_{pN} / (8\lambda)$$

where $P$ is a normal distribution with mean diameter of primary spheres $\bar{d}$, standard deviation $\sigma$, and $N$ is the total number of primary spheres in the chain. Performing the integration by making use of the properties of a normal distribution, one obtains:

$$f_{\text{poly}} = \mu \left( \bar{d}^2 \right)^{2} \left[ 1 + \sigma^2 / (\bar{d}^2) \right] (c_{mp} + (N-1)c_{bcu}) / (4\lambda)$$

The expression on the RHS, valid to an accuracy of about 2% for $N > 12$, is used in our estimate.

The mobility diameter $d_{mp}$ corresponding to the friction coefficient given in Eq. (13) is expressed implicitly by:

$$f_{\text{poly}} = \frac{\mu N \left( \bar{d}^2 \right)^{2} c_{bcu} \left[ 1 + \sigma^2 / (\bar{d}^2) \right]}{4\lambda} = f_{\text{mon}} \left[ 1 + \sigma^2 / (\bar{d}^2) \right]$$

$$= \frac{3\pi \bar{d}^2 (d_{mp})}{C(d_{mp})}$$

The value of $d_{mp}$ is slightly different from $d_{bcu}$, the mobility of the monodisperse chain of spheres, because of the term containing $\sigma^2$.

To compute $\kappa$ for the polydisperse aerosol, we need the volume equivalent diameter for the polydisperse particles, $d_{vep}$. Using the properties of the normal distribution, we find:
where $d_{ve}$ is the volume equivalent diameter of the chain with $N$ primary particles all with diameter $d_p$. The expression for the friction coefficient of the volume equivalent diameter is then given by:

$$f(d_{ve}) = \frac{3\mu d_{ve}}{C(d_{op})}.$$  \hfill (16)

From Eqs. (14) and (16), one can compute the dynamic shape factor as a function of $N$, and also using the right hand side of Eq. (14), one can express the dynamic shape factor as a function of the mobility diameter. The ratio of the dynamic shape factor of the polydisperse distribution versus the monodisperse distribution is plotted in Fig. 2. It is seen that the ratio is mostly in the range 0.97 to 0.98.

As seen from Eq. (14), the friction coefficient for the polydisperse case is proportional to $N$ so the exponent remains unchanged with a value of 1.0. The mass of the polydisperse chain can be expressed in terms of $N$ using Eq. (15) and ultimately be computed as a function of implicitly expressed in terms of $d_{ve}$ using Eq. (14). The change in the exponent $D_{in}$ from the value for the monodisperse distribution is found to be 0.003.

The above estimate is expected to provide a useful first order estimate for a small coefficient of variation $(\sigma / d_p)$; however the above estimate may not be valid for large values of the coefficient of variation. In the Chan and Dahneke analysis for monodisperse spheres, a gas molecule reflecting from one sphere can only collide with a neighboring sphere. As the polydispersity increases, the friction coefficient could be affected by reflected molecules from a large sphere hitting next nearest neighbors.

**Variable Primary Size**

Our analysis assumes that the primary sphere size is constant independent of the agglomerate size. This would be the case if the growth and shape of the primary spheres were fixed before the spheres began to form agglomerates. In reality, there may be some growth of primaries as well as sintering of primaries during the agglomeration. Rogak et al. (1993) showed that primary particle size of TiO$_2$ agglomerates increases by 28% over the mobility diameter range from 90 nm to 260 nm. Oh et al. (2004) showed that primary sphere size increases from 7 nm to 19 nm as the mobility diameter changes from 100 nm to 200 nm. In the studies of the dynamics of silver agglomerates (Shin et al. 2009a, b), the average primary particle size was determined, but the dependence of the primary size on the agglomerate size was not investigated. However, qualitatively, there was no indication of a major agglomerate size dependence. Still, it is of interest to estimate the effect of a changing primary sphere size on the agglomerate dynamics. In the analysis below, we assume a small size dependent effect corresponding to a 10% increase in the primary size as the mobility diameter increases from 100 nm to 300 nm.

We assume that the primary sphere size has a power-law dependence on the number of primary spheres in the agglomerate:

$$d_p(N_v) = d_{pc}N_v^\alpha$$  \hfill (17)

Substituting Eq. (17) into the large $N$ approximation for Eq. (1) yields:

$$f_v = \frac{c_{bcu}p}{4\lambda} d_{pc}^2 N_v^{1+2\alpha}.$$  \hfill (18)

This is to be compared with the following expression for a constant primary sphere size, $d_{pc}$:

$$f_0 = \frac{c_{bcu}p}{4\lambda} d_{pc}^2 N_0.$$  \hfill (19)

In the above, the subscript $v$ refers to the case of size dependent primary size and the subscript 0 refers to the case of constant primary size $d_{pc}$. From this analysis we see that the power law exponent $\eta$ increases by an amount $2\alpha$ for the size dependent $d_p(N)$ relative to the constant $d_{pc}$.

The value of $\alpha$ is computed from Eq. (17) assuming a 10% change in $d_p(N)$ as the cluster size increases from 36 spheres to 167 spheres. We obtain $\alpha$ equal to 0.062. This range in primary sphere sizes corresponds to the range in mobility diameter from 100 nm to 300 nm, which is the range studied by Shin et al. (2009a). In this case the exponent $\eta$ increases by 0.124, which is the opposite of our experimental observation.

In the experiments by Shin et al. (2009a), the friction coefficient was measured as a function of the mass of the agglomerates. The number of primary spheres in the agglomerates was computed assuming a constant primary diameter of 16.2 nm. This number corresponds to $N_0$. It is of interest to compute the apparent value of $\eta$ ($\eta_0$) for the model described above based on the power law dependence on $N_p$ rather than $N$. This will provide an estimate of the error in our experimentally determined $\eta$ if the primary sphere size were variable.

Equating the mass of the agglomerate with the size dependent primary sphere size to the one with the constant sphere size leads to the following relationship for the number of primary spheres:

$$N_0 = d_{pc}^3 N_v^{1+3\alpha}.$$  \hfill (20)

From Eqs. (18) and (20), one obtains the following expression for the dependence of $f_v$ on $N_0$:

$$f_v = c_{bcu}^p \frac{p}{4\lambda} d_{pc}^2 \left( \frac{d_{pc}}{d_{pc}^0} \right)^{1+2\alpha} N_0^{1+2\alpha}.$$  \hfill (21)
Based on $\alpha$ of 0.062, the apparent exponent $\eta_a$ equals 1 + $2 \alpha/1 + 3 \alpha = 0.948$. The quantity $\eta$ for the original Chan and Dahneke’s model equals 1 and the actual $\eta$ based on the increasing primary sphere size equals 1 + $2 \alpha = 1.124$. This correction would be valid over the range of particle sizes for which Eq. (17) is valid. Experimentally Shin et al. (2009a) found that the exponent $\eta_a$ decreased from a value of about 0.90 from mobility diameters smaller than 100 nm to a value of about 0.75 for larger agglomerates. This change was attributed to an enhanced flow interaction with increasing agglomerate size. We see that the effect of a size dependent primary sphere size is in the same direction as the flow effect. There is a large uncertainty in the estimated value of $\alpha$ and quantitative data are needed on the size dependence of the primary sphere size.

It is also of interest to compute the effect of an increasing primary sphere size on the dynamic shape factor. Carrying out analysis similar to that above one obtains the following expression for the ratio of the dynamic shape of the size dependent to constant primary sphere size, $\kappa_a/k_0$:

$$\frac{\kappa_a}{\kappa_0} = \frac{d_p}{d_{m}} N_v^{-\alpha}$$

(22)

The value of $d_{m}$ is taken to be 16.2 nm and this value is set equal to $d_0(N_v)$ for $N_v = 36$. This is an arbitrary but convenient choice since it leads to $\kappa_a/\kappa_0 = 1$ for $N_v = 36$, which corresponds to a mobility diameter of 100 nm. In the study by Shin et al. (2009a), the minimum mobility diameter was typically 100 nm. As $N_v$ increases to 167, the ratio decreases by 8.7%. This ratio can be computed as a function of the mobility diameter of the agglomerate for a constant primary sphere size using Eqs. (19) and (6). The results are shown in Fig. 2.

For each value of $N_v$, one can compute the mass of the agglomerate by making use of Eq. (17). This together with the calculation of the mobility diameter enables one to compute the mass-mobility diameter scaling exponent $D_m$. One finds for the size dependent primary sphere size, the $D_m$ is 0.081 larger than the baseline case.

DISCUSSION AND SUMMARY

In summary, four non-ideal effects are estimated as perturbations to the Chan and Dahneke model. The change in the exponents $D_m$ and $\eta$ arising from polydispersity and from necking are negligible with changes less than 1%. Alignment in the electric field results in about a 4% change in both exponents in the direction of the experimental results relative to the model prediction. The estimate is an upper bound estimate, since the perturbed case for the 300 nm mobility diameter is fully aligned. Partial alignment is more likely the case unless the agglomerate is more than a micrometer long.

The case of the variable primary sphere size is more dramatic but also more uncertain than the other perturbations. Assuming a 10% increase in the primary sphere size as the mobility diameter of the chain increases from 100 nm to 300 nm, one estimates about a 10% increase in both $D_m$ and $\eta$. In the case of $\eta$ the direction of the deviation is the opposite of the experimental observation. These estimates are based on the number of primary spheres in the chain.

Experimentally the number of primary spheres is determined from the mass of the agglomerate assuming a constant primary sphere diameter. The apparent exponent $\eta$ based on a 10% variability in the primary sphere size is about a 5% less than the apparent exponent assuming a constant primary sphere size. This is a significant effect relative to the observed 15% decrease in $\eta$ (Shin et al., 2009a) as the agglomerate size increases from the free molecular regime into the transition regime. This observed change in $\eta$ (Shin et al., 2009a) is attributed to a flow interaction between the primary spheres.

While the magnitude of this effect and its relevance to understanding the flow effect are significant, the direct experimental evidence for a systematic variation of the primary sphere size with the size of the agglomerate for silver agglomerates does not exist. The estimated effect is based on the uncertainty in the measurement of the primary particle size and the uncertainty in the estimate is on the order of $\pm 100\%$ of the value.

While polydispersity has a negligible effect on the exponents, it has the dominant effect on the dynamic shape factor. It results in about a 14% decrease in the dynamic shape factor for agglomerates with a mobility diameter approaching 300 nm. It is of interest to apply these corrections to the dynamic shape factor for the prediction of the model of Meakin et al. (1989), since this model includes a more realistic fractal structure of the agglomerate and closer agreement with experimental results.

In Fig. 3, experimental data (Kim et al., 2008) are compared with the model predictions. In the experiment, mass of silver agglomerates was measured in mobility size range of 50 to 300 nm using a DMA together with APM. The average primary particle size of silver agglomerates

Fig. 3. Dynamic shape factor as a function of $d_m$ before and after adjustment of Meakin et al. considering non-ideality.
used in the experiment is 16.2 nm. It is seen in Fig. 3 that the modified Meakin et al. results are in much better agreement with the measured results than the original predictions. We have not included the effect of the variable primary sphere size because of the large uncertainty in this effect.

Results from this study will hopefully motivate studies to extend existing models to quantitatively assess these effects and to expand the database for the friction coefficient of real particles.

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